

A sodium and silica-containing compound such as $\text{Na}_2\text{O} \cdot (\text{SiO}_2)_{3.38}$ or Na_2SiO_3 or $(\text{NaO})_2\text{Si}(\text{CH}_3)_2$ can be used as a precursor for SiO_2 and Na_2O . Other precursors for SiO_2 include silicic acid and colloidal SiO_2 . The precursors for CaO include the calcium salt of a C_1 to C_4 alkanolic acid, preferably calcium formate, $\text{Ca}(\text{O}_2\text{CH})_2$, and, when HNO_3 is used to control pH, $\text{Ca}(\text{NO}_3)_2$. Precursors for P_2O_5 and Na_2O , are the sodium phosphates, Na_3PO_4 , Na_2HPO_4 , NaH_2PO_4 , $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$ and the sodium phosphites Na_3PO_3 , Na_2HPO_3 and NaH_2PO_3 . Preferred is the sodium phosphate $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$. Other precursors for P_2O_5 include H_3PO_4 and the ammonium salts equivalent to the above sodium salts. The precursors for B_2O_3 include the sodium borates, which also provide Na_2O . Preferred is $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$. precursors for Na_2O include the sodium salts mentioned above as well as the sodium salt of a C_1 to C_4 alkanolic acid, preferably sodium formate, and, when HNO_3 is used to control pH, NaNO_3 . The introduction of ions such as SO_4^{2-} and Al^{+3} that would immediately form precipitates with other ions present should be avoided. Other ions that enhance biological growth can also be introduced into the solution. These ions include Mg^{+2} ; see Jaffe "Metabolic Degenerative and Inflammatory Diseases of Bones and Joints", Lea and Febiger, Phila. (1972) page 124 and following. Should K_2O be desired as a component of the glass, it can be included in the precursor solution as KHCO_3 , KNO_3 or $\text{KOC}(\text{O})\text{R}$.

The aqueous solution compositions of this invention have a pH typically below about 5. Preferred acids for pH control are those which decompose cleanly on heating and leave no carbon residue that would require prolonged ignition. Such clean deposition is a general requirement for an acid whose salts are used or which is used in the free state. Enough acid is added to the solution to achieve the desired pH. Acids that meet the requirements of relatively high volatility and clean decomposition include nitric acid and C_1 to C_4 alkanolic acids, including any acid whose calcium and sodium salts are used in making up the solution or dispersion. Since these salts are preferably formates, the most preferred acid is formic acid. For formic acid and nitric acids the pH will be at most about 3.8, and preferably about 3.3 to 3.8. For acetic acid, propionic acid, and the butyric acids the pH will be at most about 4.6, and preferably about 4.1 to 4.6. The optimum pH for any particular glass precursor composition can readily be determined by simple experiment.

In the actual coating operation, the particulate support to be coated is intimately mixed with a freshly prepared solution of glass precursors with agitation and preferably with gentle grinding. In the laboratory, mixing, agitation, and grinding are conveniently accomplished with a mortar and pestle. The wet solid can then be air-dried to remove all or part of the water; spray-drying techniques being preferred. The dried solid is then heated at a temperature high enough to remove any remaining water, volatilize and/or decompose any remaining formic acid, and convert the component of the coating medium to the desired glass. This temperature is usually about 600°C . to 1550°C . although somewhat lower temperatures can sometimes be employed effectively.

A convenient method for making up the coating solution to minimize the chance of precipitation is to make up two solutions, the first containing calcium formate and sodium formate, if any, and the second containing

sodium silicate and whatever sodium phosphate and/or sodium borate is to be used. Formic acid is then dissolved in either solution, and the two solutions are mixed rapidly with good agitation. The amount of formic acid to be used can be easily determined by simple experiments with aliquots of the two solutions.

The relative amount of each inorganic precursor dissolved in the coating medium will be equivalent to the relative amount of the corresponding inorganic component necessary to form the desired glass. Usually, the concentration of precursors will be about 100 g to 200 g per liter of solution. At lower concentrations, an unnecessarily large amount of water has to be evaporated in the heating step; at higher concentrations there is a greater tendency to form precipitates. The support particles contacted with said precursors will vary in size and concentration according to the weight and/or volume relationship desired in the glass-coated support product. Multiple coating/drying/sintering steps can also be employed.

The biologically active glasses that are made by the precursor solution process of this invention are well accepted as components in biomedical products including devices, prostheses, replacement parts and implants for the body. The utility of the supported biologically active glass of this invention is at least coextensive with that of unsupported biologically active glass. In addition, the supported glass has strength/smoothness/rigidity and density advantages—balanced with homogeneous composition characteristics—not heretofore possible.

Coated supports can be sintered and/or fused onto nearly any compatible substrate to form large or small devices of almost any geometry. The coated supports can also be molded or cast to form biomedical devices comprised solely of the support and glass described herein in a uniform, homogeneous and body-compatible matrix.

The requirements met by biomedical materials made from the supported glass of this invention are as follows: (1) their properties approximate those of the body part that they replace or in which they are incorporated; (2) they are accepted by the living host without adverse reactions such as inflammation or toxicity; (3) they form in vivo bonds with host tissues; and (4) their implantation does not cause the formation of more than a relatively thin "capsule" at their interface with the host's body part.

EXAMPLE 1

Two solutions were made up as follows: Solution I contained 56.9 g of calcium formate, 6.1 g of sodium formate, and enough water to make 500 ml of solution; its pH was 6.6. Solution II contained 32.0 g of $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$, 158.5 g of $\text{Na}_2\text{O} \cdot (\text{SiO}_2)_{3.38}$ as an aqueous 37.1% solution, and enough water to make 500 ml of solution; its pH was 10.9.

To 37.5 ml of solution I was added 5.3 ml of formic acid, and the resulting solution was added rapidly with good stirring to 37.5 ml of solution II. The combined solution was added slowly to 155 g of alumina in a mortar as the mixture was stirred with a pestle. The alumina was obtained by calcining $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ (Alcoa C30BF). Stirring was continued until the mixture was uniform. The product was fired at 1200°C . in a muffle furnace overnight. The solid was again surface-treated by the method described in this paragraph, to give a biologically active glass-coated alumina that had a sur-